ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 5251–5262

polymer

www.elsevier.com/locate/polymer

Reactive compatibilization of blends of polybutyleneterephthalate with epoxide-containing rubber. The effect of the concentrations in reactive functions

P. Martin[a,*], C. Gallez[a], J. Devaux[a], R. Legras[a], L. Leemans[b], M. van Gurp[b], M. van Duin[b]

[a]*Laboratoire des Hauts Polymères, Université Catholique de Louvain, 1, Place Croix du Sud, 1348 Louvain-la-Neuve, Belgium*
[b]*DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands*

Received 29 October 2002; received in revised form 27 May 2003; accepted 5 June 2003

Abstract

The influence of the functional groups concentrations on the reactive compatibilization of polybutylene terephthalate (PBT)/epoxide-containing rubber blends has been investigated by using various PBT and ethene-(methyl acrylate)-(glycidyl methacrylate) terpolymer (E-MA-GMA) grades. The reactivity of the rubber phase was modified using different strategies, including the use of commercial terpolymer grades, modification of E-MA-GMA or diluting E-MA-GMA terpolymers with non-reactive ethene-(methyl acrylate) (E-MA) copolymer. The reactive blends were analyzed amongst others by electron microscopy and fractionation experiments. It was shown that the final particle size is directly related to the amount of copolymer formed in situ at the blend interface, i.e. chain area density Σ. A value of approximately 0.05 chains/nm^2 for Σ is necessary to suppress dynamic coalescence and to obtain very fine dispersion (<0.2 μm). This requires a sufficiently high concentration in reactive functions at the interface vicinity. In this context, the time required for equilibrium morphology is rather independent of the GMA content in the terpolymer but is, however, intimately related to the PBT chain ends concentration. Investigation of PBT/(E-MA-GMA/E-MA) ternary blends revealed unambiguously that the formation of the copolymer at the interface is not controlled by the diffusion of the reactive chains towards the interface. The performed experiments offer new opportunities for modulating the final morphology and the properties of the PBT/rubber blends.

Keywords: Polybutylene terephthalate/rubber polymer blends; Epoxide functions; Reactivity

1. Introduction

Polymer blending is nowadays one of the most attractive routes to develop rapidly new materials and to produce them at low costs [1]. Since most polymers are immiscible, polymer blends consist generally in two-phase systems. Such materials are very promising, because each constitutive phase keeps its intrinsic properties. Unfortunately, such blends exhibit usually poor mechanical properties. This is due to the low polymer compatibility, which leads to a coarse unstable morphology and to a lack of interfacial adhesion. To obtain high performance materials, the compatibilization of the blend has to be achieved. This process consists in adding appropriate block or graft copolymers to the blend components during processing. The different blocks of the copolymers have affinity for either of the two blend phases. The efficiency of block and graft copolymers in reducing the interfacial tension and improving the interfacial adhesion has been extensively discussed [2–6]. These additives can be premade or generated in situ using a reactive blending process, i.e. reactive compatibilization. This later has the advantage to be more straightforward and to form the compatibilizer where it has to be localized, i.e. at the interface.

The kinetics of the interfacial reaction is expected to play a major role in polymer blends prepared by reactive processing, since it will decide on the amount and the structure of the in situ formed compatibilizer, and ultimately on the properties of the polymer blends [7,8]. It is now well established that the kinetics of the interfacial reaction is intimately related to the nature of reactive functions and to the molar concentration of the reactive groups present in the interface vicinity [9,10]. In this context, different theoretical

---

[*] Corresponding author. Tel.: +32-10-473088; fax: +32-10-451593.
E-mail address: martin@poly.ucl.ac.be (P. Martin).

0032-3861/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0032-3861(03)00499-3

models distinguishing various kinetic regimes appeared recently in the scientific literature [11–14].

The efficiency of reactive compatibilization of immiscible polymer pairs has already been studied in relation to the nature of the reactive species [8,15–17]. Pagnoulle [8] has studied the compatibilization of blends of styrene–acrylonitrile copolymer (SAN) and ethylene–propylene rubber grafted with maleic anhydride (EPM-*g*-MA) using reactive SAN chains, containing primary amine or carbamate functions. Carbamate species are amine precursors, since they decompose at high temperatures. It was shown that the structure as well as the stability of the copolymer formed at the interface during processing is intimately related to the reactivity of the SAN chains. Large differences in the morphology and in the final blend properties were observed [8]. Similar conclusions were also obtained by Orr et al. for polystyrene/polyisoprene systems [16] and by Chareonsirisomboon et al. for polyamide 6/polysulfone blends [17]. In addition to the intrinsic reactivity of the reactive species, the blend compatibilization is also intimately related to the content of the reactive groups. For instance, De Roover et al. [18] have studied the effect of the content of maleic anhydride (MA) grafted onto polypropylene (PP-*g*-MA) on the average size of the PP phases dispersed in poly(*m*-xylene adipamide) PA(mxD,6). This size decreases rapidly with increasing content of grafted anhydride. However, beyond a critical content, the particle size levels off. Such a behavior was attributed to the fact that the copolymer formed at the interface becomes rich enough in PA(mxD,6) for leaving the interface in favor of the polyamide phase, i.e. micelle formation. Similar results were obtained by other authors [19–22]. For maleinated polystyrene (SMA)/polyamide 12 (PA-12) blends, Steurer and Hellmann have demonstrated that the interfacial grafting turns out to be incomplete and non-random [22]. In other words, not all PA-12 chains are grafted and not all SMA chains are collecting the same number of PA-12 grafts. For high content in low molecular weight PA chains, the SMA-*g*-(PA-12) graft copolymer can leave the interface leading to a renewal of the interface and a constant reactivation of the interfacial reaction.

The current work is part of a series of studies on the impact modification of polybutylene terephthalate (PBT) by terpolymers of ethylene (E), methyl acrylate (MA) and glycidyl methacrylate (GMA). It has already been shown that PBT/E-MA-GMA blends exhibit a very complex reactivity [23]. Two reactions appear to take place simultaneously during melt processing viz. (i) compatibilization due to interfacial reaction between carboxyl PBT chain ends and terpolymer epoxide groups, resulting in the formation of E-MA-GMA/PBT graft copolymer and (ii) rapid crosslinking of the rubber phase due to the presence of both hydroxyl and epoxide groups on E-MA-GMA chains. This competition between compatibilization and crosslinking is dependent on the type of terpolymer, i.e. virgin or modified E-MA-GMA. This latter rubber grade was synthesized in a preliminary step by melt mixing virgin E-MA-GMA with calculated amounts of low molecular weight acid in order to modify part of the epoxide groups. Two different blending mechanisms were distinguished depending on the type of used E-MA-GMA [24]. In the case of terpolymer modified with acid, secondary hydroxyl groups are present in the rubber phase from the beginning. Competition between compatibilization of the blend and crosslinking of the rubber place takes place upon melting and proceeds homogeneously throughout the whole E-MA-GMA particles, which affects both the dispersion and coalescence processes. For PBT blends with unmodified terpolymer, competition between the two types of reactions is somewhat delayed. In the first stages of mixing, compatibilization occurs first, which initiates crosslinking at the interface from where it proceeds from the interface to the core of the rubber particles. The morphology development is thus more complex and the dispersed particles will probably have a large heterogeneity and may even have a core-shell type structure. All these phenomena result in a very complex processing/morphology interrelationship and probably also affect the final blend properties.

A recent study has highlighted the possibility to control such complex systems by an adequate choice of the processing conditions and the PBT matrix viscosity [25]. In this work, the influence of both PBT and rubber phase reactivity on the compatibilization of PBT/rubber blends has been investigated. The reactivity of the rubber phase was modified using different strategies, including the use of commercial terpolymer grades, modification of E-MA-GMA or diluting E-MA-GMA terpolymers with non-reactive E-MA copolymers. The performed experiments offer new opportunities for modulating the final morphology and the properties of the PBT/rubber blends.

2. Experimental

2.1. Materials

Various PBT grades of different molecular weight and with different end group concentrations were used in this study. All grades were supplied by DSM. Their main characteristics, such acid and hydroxyl chain ends concentrations and relative viscosities are given in Table 1. Each PBT grade is identified by its molecular mass (H: high, M: medium and L: low) and its carboxyl chain end content.

The different rubbers used in this study are reported in Table 2. Lotader AX8900 and AX8920 (noted E-MA-GMA8 and 1, respectively) were purchased from Elf-Atochem Co. Their compositions are 68 wt% E, 24 wt% MA and 8 wt% GMA and 71 wt% E, 28 wt% MA and 1 wt% GMA, respectively. Their melt flow index is 6 g/10 min at 190 °C under 325 g. The number average and weight average molecular weight for Lotader AX8900 were 10 and 31 kg/mol, respectively. The average number of epoxide functions per terpolymer chain is equal to 5–6

Table 1
Characteristics of the PBT grades

PBT grade	[–COOH] (μeq/g)	[–OH] (μeq/g)	Relative viscosity η_r in m-cresol	Mn (kg/mol)
L-PBT45	45	66	1.85	16.1
L-PBT7	7	109	1.85	16.1
M-PBT49	49	31	2	19.8
H-PBT42	42	10	2.4	30.9
H-PBT10	10	60	2.4	31.4

functions per chain. Lotril 28MA07 (E-MA) was also purchased from Elf-Atochem Co. and is rather similar to Lotader AX8900, viz. a composition of 30 wt% MA content and MFI = 6 g/10 min at 190 °C under 325 g. Despite some differences in the chemical structure, preliminary experiments have demonstrated that E-MA-GMA and E-MA are fully miscible.

Various modified E-MA-GMA grades were synthesized in the melt by mixing E-MA-GMA AX8900 with different amounts of *para-t*-butylbenzoic acid according to the procedure previously described [23]. In this study, four modified E-MA-GMA with modification levels of 23, 48, 73 and 93% were used after purification.

2.2. Processing

Prior to processing, all materials were dried overnight at 25 °C under vacuum. Although standard common PBT drying conditions are 125 °C under vacuum, preliminary experiments comparing both drying conditions have not shown any effect on PBT degradation and on the compatibilization process for experiments performed in the internal mixer [24].

PBT/rubber binary blends were prepared at 250 °C using a Brabender WE 50H internal mixer. The atmosphere in the mixer was controlled by purging with nitrogen gas. Blends compositions were 80/20 (w/w) PBT/rubber. Except when specified differently, the PBT pellets were melted for 1 min at 30 rpm prior to addition of the rubber powder. Immediately after introduction of the rubber powder, the rotation speed was increased to 90 rpm. The zero time was taken when all the rubber was introduced and the total mixing time was fixed at 18 min. At different times after rubber addition, samples were rapidly withdrawn from the mixing cavity and quenched in liquid nitrogen in order to stop the interfacial reactions and freeze in the morphology.

In the case of PBT/(E-MA-GMA8/E-MA) ternary blends, the blending procedure was modified in order to ensure homogeneous dispersion of the E-MA-GMA8 reactive chains in the E-MA. For this purpose, E-MA-GMA8/E-MA dry blends of various compositions were first melt blended at 250 °C and 30 rpm for 1 min. After this preblending, the PBT pellets were added to the rubber phase for 1 min at 30 rpm. The amount of PBT was calculated to achieve a blend composition of 80/20 (w/w) PBT/rubber. After complete introduction of the PBT, the screw speed was increased to 90 rpm. This moment corresponds to the zero mixing time.

Table 3 presents the different PBT/rubber blends performed in this study.

2.3. Microscopy

The blend morphology was examined by Transmission Electron Microscopy (TEM). For this purpose, samples were ultra-microtomed in thin films of approximately 90 nm at −80 °C in order to avoid deformation of the dispersed phase particles. The microtomed cuts were stained for 6 min with RuO_4 for 1 h before examination with a Philips EM 301 microscope.

After examination, the morphology was quantified by image analysis. For each sample, at least 200 particles were measured and both the volume and the number average diameters were estimated on a Macintosh computer using the public domain NIH Image program (developed at the US National Institute of Health).

Table 2
Characteristics of the rubber materials

Code	Original rubber	Modification level (%)	Epoxide content (wt%)
E-MA	Lotril 28MA07	0	0
E-MA-GMA8	Lotader AX8900	0	8
E-MA-GMA1	Lotader AX8920	0	1
23% modified E-MA-GMA	Lotader AX8900	23	6.2
48% modified E-MA-GMA		48	4.2
73% modified E-MA-GMA		73	2.2
93% modified E-MA-GMA		93	0.6

Table 3
Description of the PBT/rubber (80/20, w/w) blends and values of the COOH/epoxide concentration ratio

Matrix	Rubber phase	COOH/epoxide ratio
L-PBT45	E-MA	45/0
	E-MA-GMA8	0.32
L-PBT7	E-MA-GMA8	0.05
H-PBT42	E-MA	42/0
	E-MA-GMA8	0.30
H-PBT10	E-MA-GMA8	0.07
M-PBT49	E-MA	49/0
	E-MA-GMA8	0.34
	E-MA-GMA1	2.73
	E-MA/E-MA-GMA8 (75/25, w/w)	1.36
	E-MA/E-MA-GMA8 (50/50, w/w)	0.68
	E-MA/E-MA-GMA8 (25/75, w/w)	0.45
	23% modified E-MA-GMA8	0.44
	48% modified E-MA-GMA8	0.65
	73% modified E-MA-GMA8	1.26
	93% modified E-MA-GMA8	4.87

2.4. Fractionation

A procedure was developed for removing free PBT chains from the PBT/rubber blends. Approximately 1 g blend was introduced in 30 ml of pure trifluoroacetic acid (TFA), a good selective solvent for PBT, and stirred at room temperature for 1 h in order to dissolve the PBT phase. A milky emulsion was obtained and ultra-centrifugated at 14 °C and 25,000 rpm using a Beckman L7-65 ultracentrifuge. After 1 h 45 min, clear separation was achieved. The grafted rubber particles were concentrated as a white layer at the top of the centrifugation tube. The clear TFA solution was carefully removed and the dissolved PBT was precipitated in methanol, filtrated over a 0.5 μm PTFE filter, washed with methanol and dried at 30 °C under vacuum for 24 h to yield fraction $P1$. The rubber phase was dispersed again in 30 ml TFA and stirred for 45 min at room temperature. A second ultra-centrifugation was performed for 1 h 45 min at 8 °C and 28,000 rpm. Once again, the TFA solution containing free PBT was carefully separated from the rubber phase, precipitated and worked up to form fraction $P2$. This fraction represents only approximately 3 wt% of the total amount of material. Complete recovery of non-grafted PBT was achieved after the second washing step, since no additional free PBT was obtained when a third separation was carried out. Total amount of free PBT is equal to the sum of fractions $P1$ and $P2$ and is noted P.

After separation, the rubber phase was stirred in chloroform ($CHCl_3$) at 50 °C for 1 h and filtrated. Hot $CHCl_3$ is a selective solvent for both E-MA and E-MA-GMA. An insoluble fraction, called C, was recovered. The free rubber was precipitated from the $CHCl_3$ solution in methanol, filtrated and dried for 24 h at 30 °C under vacuum, yielding fraction R.

The weights of the initial sample and of the different fractions were precisely measured. Due to the large number of tricky experimental steps, some material was lost. Still, the mass recovery remained always above 90%. The amount of grafted PBT was estimated by comparison of the initial PBT content, which was equal to 80 wt% for all blends, with the PBT amount recovered in fractions $P1$ and $P2$.

Each separation was performed on at least two blend samples. Different batches of modified E-MA-GMA were produced and used successively for blending with PBT leading to truly duplicate polymer blends. The reported results correspond to mean values of all these separations. The standard deviation for each blend fraction $P1$, $P2$, R and C was in all cases below 15%.

Besides the weight of each fraction also its composition was quantitatively determined with Raman spectroscopy.

2.5. Spectroscopy

Raman spectra were recorded at 25 °C on a Labram confocal laser Raman spectrometer from Dilor S.A. in the spectroscopic mode. The excitation wavelength was 632.8 cm^{-1} from a He–Ne laser source. The pinhole aperture and the entrance slit were both fixed to 1000 μm, which resulted in a large analyzed volume of samples. A grating of 1800 grooves/mm was used and the spectra were recorded on a CCD detector. Spectra were centered on 2900 cm^{-1}. Each spectrum was the average of five accumulations of 60 s.

PBT and E-MA-GMA can be distinguished and separately quantified using the region of 2500–3250 cm^{-1}. A previously developed calibration curve was used [23].

2.6. Molau's tests

The so-called Molau's test measures the stability of a dispersion. PBT/rubber (80/20, w/w) blends were dissolved in trifluoroacetic acid, a selective solvent of PBT. Dissolution was performed under moderate stirring for 12 h. After this delay, the solution was left at rest for 2 days. If the milky aspect because of the dispersed rubber particles in emulsion remains after this time, it is concluded that the dispersed phase is stabilized, that witnesses compatibilization by copolymer. Otherwise, the large rubber particles coagulate and give a white skin on the top of the solution.

2.7. Chain area density

Recently, Fischer and Hellmann carry out a very convenient method based on a statistical analysis in order to calculate the composition, molar mass and structure of the graft copolymers formed at the blend interface [26]. Unfortunately, such an approach is not applicable in the present case, since two chemical reactions occurs simultaneously during the melt processing, i.e. interfacial grafting and rubber phase crosslinking. As a consequence, the specie formed at the blend interface is not a simple

(E-MA-GMA)-*g*-PBT graft copolymer but rather a complex structure containing crosslinked E-MA-GMA chains and PBT grafts. As no quantitative data about the rate of rubber crosslinking and the density of the formed network are available, the rigorous and precise characterization of the rubber chains connected to the PBT grafts at the interface remains impossible.

In this context, the only way to obtain more insights about the interface composition is to normalize the amount of grafted PBT to the corresponding available interfacial area. In other words, one has to calculate the average area A occupied by a copolymer chain at the blend interface [27–29]. Within the limits of the assumption that all the compatibilizer graft copolymers are and remain at the interface, Paul and Newman [30] proposed to express A by

$$A = \left(\frac{6}{D_n}\right)\Phi_d \frac{M}{N_{av}W} \qquad (1)$$

where M is the number average molecular weight of the compatibilizer, W is its wt/vol content, N_{av} is the Avogadro number, D_n is the number average diameter and Φ_d is the volume fraction of the dispersed rubber phase. In the present study, M and W are unknown since the graft copolymer cannot be isolated and therefore characterized. As a rough approximation, the molecular weight of the original PBT and the amount of grafted PBT have been used in Eq. (1). M and W are thus underestimated, this error being compensated by the fact that A depends on the ratio of these parameters [8]. The value $\Sigma = 1/A$ represents the chain area density, i.e. the number of PBT grafts per square nm of interface.

3. Results and discussion

3.1. PBT chain ends concentration

In order to investigate the effect of the PBT matrix reactivity on the morphology and the interfacial properties of the PBT/E-MA-GMA blends, PBT grades with similar molecular mass but different carboxyl chain end concentrations were used (see Table 1). Hydroxyl PBT end groups are expected to be less reactive or not reactive at all towards E-MA-GMA rubber at 250 °C [24]. Fig. 1a–d displays TEM micrographs of L-PBT7/E-MA-GMA8 and L-PBT45/E-MA-GMA8 (80/20, w/w) blends after 30 s and 18 min of mixing. Whatever the PBT phase and the mixing time, all blends exhibit a matrix-droplet morphology consisting in a PBT matrix with dispersed E-MA-GMA particles. At the same mixing time, no marked difference in the size of the rubber particles was observed between the two systems, i.e. L-PBT7/E-MA-GMA8 and L-PBT45/E-MA-GMA8 (80/20, w/w) blends. In both cases, the morphology becomes finer as the mixing time increases. Except perhaps for the size of the dispersed phase particles, the other blends used in this study display all a similar matrix-droplet microstructure, so that the images from TEM observations will be omitted for brevity reasons. Figs. 2 and 3 present the evolution of the number average diameter, D_n, of the dispersed phase particles as a function of mixing time for PBT/E-MA-GMA8 (80/20, w/w) blends containing L-PBT45, L-PBT7, H-PBT42 and H-PBT10. For blends containing highly reactive PBT, the number average diameter of the dispersed phase particles decreases as a function of time from 0.6 to 0.32 μm for L-PBT45 and from 0.35 to 0.12 μm for H-PBT42. No further change of the diameter of the dispersed particles was observed after 2 min of mixing. In agreement with previous results [25], the final morphology was also determined by the matrix viscosity. The highest the PBT molecular weight, the finest the morphology. For blends containing low reactive PBT, i.e. L-PBT7 and H-PBT10, the development of the blend morphology proceeds more slowly. A stable morphology was obtained after only approximately 8 min of mixing whatever the PBT molecular mass. It is important to note that, for a given PBT molecular mass, the initial (< 1 min) but also the final (> 10 min) morphologies are independent of the PBT reactivity.

Molau's tests showed that blends containing H-PBT42 and L-PBT45 give stable emulsions when they are dissolved in TFA except at very short mixing times. For the blends processed for 30 s at 90 rpm, partial flocculation of the rubber particles was observed with a thin white floating layer at the top of the solution. For blends containing low reactive PBT, i.e. H-PBT10 and L-PBT7, stable emulsions were only obtained for the samples produced at long mixing times, i.e. higher than 6 min of mixing.

The different L-PBT/E-MA-GMA samples were also characterized using the developed separation procedure (Table 4). Taking into account for the experimental error, no difference between the two L-PBT blends was observed after 30 s of mixing, for the amount of free PBT chains P, the amount of free rubber chains R, the amount and the composition of the insoluble fraction C. The amount of L-PBT chains grafted to the rubber particles (calculated as $80 - P$) is relatively small, i.e. 2.7% for L-PBT45 and 0.8% for L-PBT7, suggesting that the interfacial reaction has only occurred to a small extent after 30 s of mixing. This is in agreement with the results of the Molau's tests and the relatively low copolymer interfacial coverage, i.e. the low Σ values. The effect of the PBT reactivity seems therefore to be relatively small in the early stages of the mixing, although the amount of grafted PBT is already higher for L-PBT45. After 8 min of mixing, the blends containing L-PBT45 have the highest amount of grafted PBT and the highest interfacial copolymer coverage. In the same way, the insoluble fraction is less rich in E-MA-GMA chains. In other words, the higher the concentration of carboxyl PBT chain ends, the faster the interfacial reaction. It is also interesting to note that the amount of free rubber decreases as the carboxyl content of the PBT chains increases. Similar

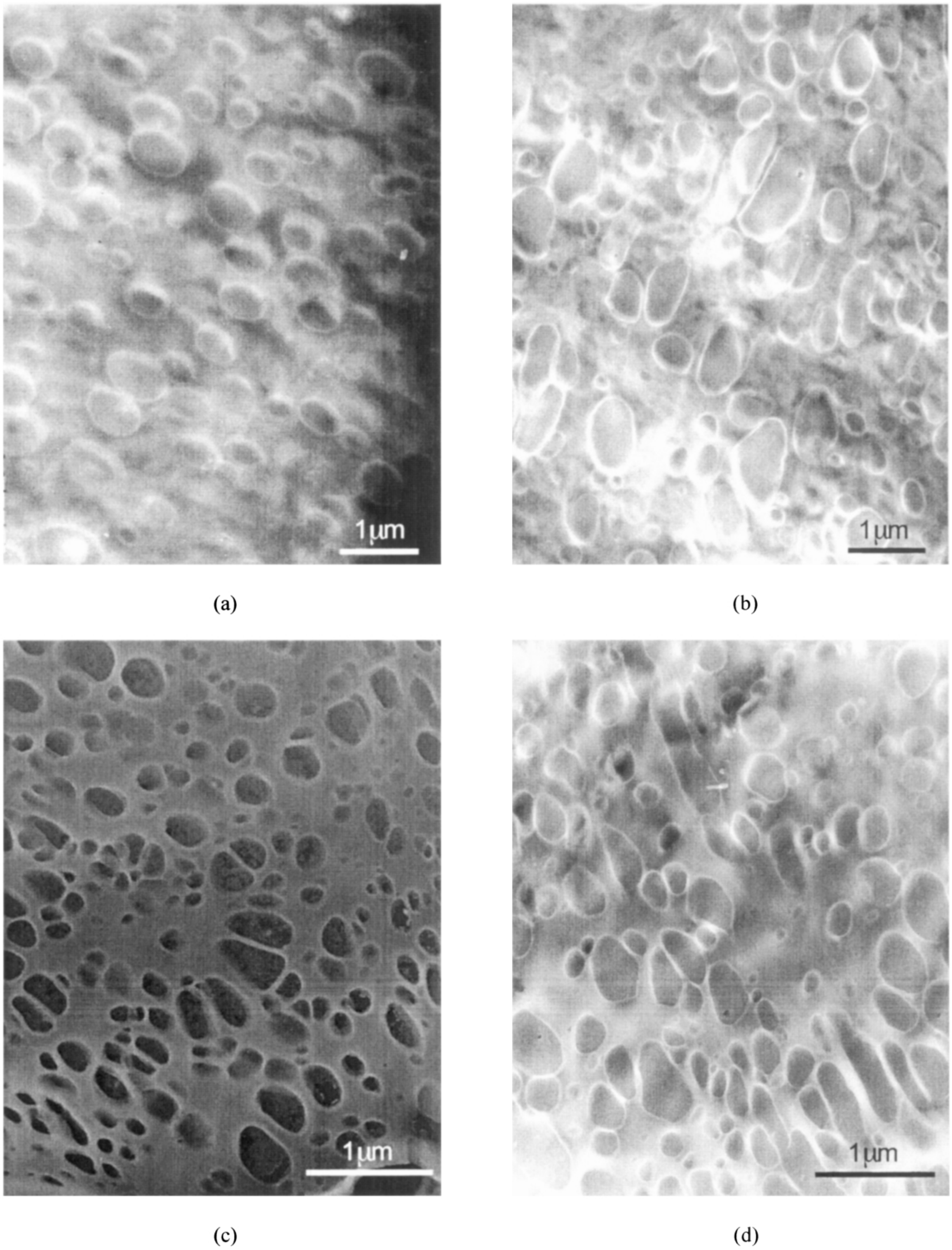


Fig. 1. TEM micrographs of different L-PBT/E-MA-GMA8 (80/20,w/w) blends after 30 s and 18 min of mixing (250 °C and 9 rpm): (a) L-PBT7/E-MA-GMA8 after 30 s; (b) L-PBT45/E-MA-GMA8 after 30 s; (c) L-PBT7/E-MA-GMA8 after 18 min and (d) L-PBT45/E-MA-GMA8 after 18 min.

conclusions can be drawn for H-PBT/E-MA-GMA8 blends as also shown in Table 4.

In a previous paper [25], we suggested that the morphology development in PBT/E-MA-GMA blends can be schematically divided in two regimes due to the low reactivity of the carboxyl/epoxide pair (Scheme 1). In the early stages of blending, the morphology development is essentially governed by the physical processes of dispersion and coalescence. As the mixing time increases, the effects of the chemical reactions, i.e. blend compatibilization and

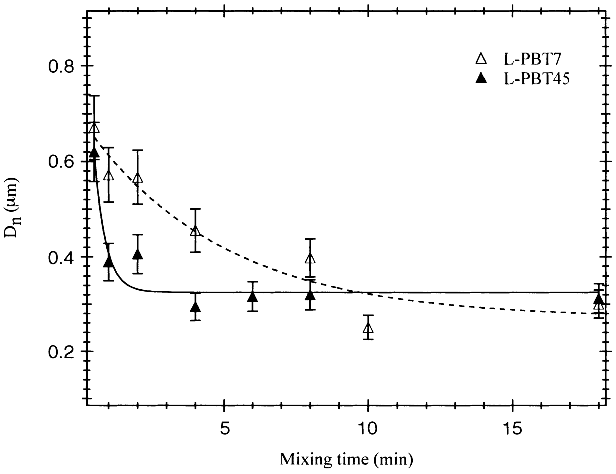


Fig. 2. Influence of the PBT reactivity on the evolution of the rubber particle size as a function of the mixing time for L-PBT/E-GMA8 (80/20, w/w) reactive blends.

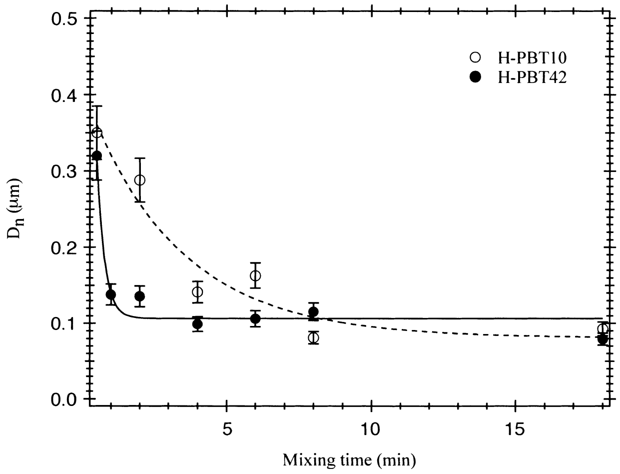


Fig. 3. Influence of the PBT reactivity on the evolution of the rubber particle size as a function of the mixing time for H-PBT/E-MA-GMA8 (80/20, w/w) reactive blends.

rubber phase crosslinking, become more and more important leading to a further modification of the blend morphology. This scheme is confirmed by the results discussed above. In the early stages of blending (< 1 min), the interfacial coupling reaction between the PBT carboxyl chain ends and the rubber epoxide functions has only proceeded on a small extent so that the morphology development is essentially controlled by physical factors such as shear rate or phase viscosity. It is therefore not surprising that, whatever the PBT molecular mass, the number average diameter of the dispersed phase particles was almost independent of the matrix reactivity. Crosslinking of the rubber phase also occurs during this short period of time as shown by the recovered amounts of free E-MA-GMA *R* and of insoluble fraction *C*. As the mixing time increases, the effect of the chemical reactions should become more and more pronounced. According to several authors [9–15], the rate of interfacial reaction in case of epoxide/carboxyl pair should be defined as:

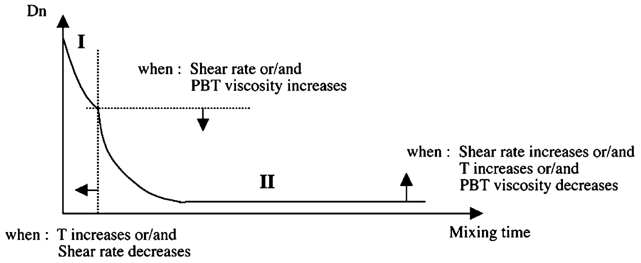
$$v = k_{AB}[A][B] \tag{2}$$

where k_{AB} is the kinetic constant for the reaction between the chemical functions *A* and *B* and [*A*] and [*B*] are the concentrations of reactive functions *A* and *B*, respectively, in the interface vicinity, i.e. the interphase volume (= interfacial area × interphase thickness). In this case, the amount of epoxide groups present in the system was the same for each experiment. As the concentration of PBT carboxyl chain ends is increased, the rate of interfacial reaction is therefore expected to increase according to Eq. (2). As a consequence, the formation of E-MA-GMA/PBT graft copolymer and the subsequent crosslinking of the rubber phase take place more rapidly in case of PBT/E-MA-GMA8 blends containing L-PBT45 and H-PBT42 (Table 4). Such differences explain why the morphology development is more rapid for PBT with the highest concentration in carboxyl chain ends (Figs. 2 and 3).

As shown in Figs. 2 and 3, the concentration of carboxyl end groups affects the time required to obtain a stable dispersion, but not the size of this final dispersion. To explain such a surprising result, the copolymer area density, Σ, has to be considered. It is now well established that a minimum interfacial coverage is required to prevent both dynamic and static coalescence of the dispersed particles and to achieve a fine and stable morphology. According to Macosko et al. [31], this minimum value is around $\Sigma = 0.02$ chain/nm^2. Similarly, experimental and theoretical values of $\Sigma = 0.02$ chain/nm^2 and 0.09 chain/nm^2 were

Table 4
Amount and composition of the different fractions and interfacial copolymer coverage for L-PBT/E-MA-GMA (80/20, w/w) and H-PBT/E-MA-GMA (80/20, w/w) blends after different mixing times

Mixing time (min)	Matrix	*P* (wt%)	*R* (wt%)	*C* (wt%)	Composition *C* (% rubber)	Σ (chain/nm^2)
0.5	L-PBT45	78.3	11.6	7.85	99	0.013
	L-PBT7	79.2	10.5	7.35	99	0.015
8	L-PBT45	74.0	2.4	15.5	65	0.520
	L-PBT7	78.0	4.3	13.8	97	0.049
1	H-PBT42	75.0	2.7	11.8	74.0	0.067
	H-PBT10	77.9	4.6	6.4	86.2	0.042
8	H-PBT42	53.2	0.15	38.7	45.3	0.386
	H-PBT10	68.7	0.9	21.0	68.6	0.068



Scheme 1. Schematic representation of the mixing process. I: ‘physics-controlled’ regime; II: ‘chemistry-controlled’ regime. As schematically presented, the transition between the two regimes is dependent on the processing conditions.

found by Jeon et al. for polystyrene/poly(methyl methacrylate) blends [32]. In this work, a value of approximately 0.05 chain/nm^2 seemed to be necessary to obtain the final domain size. Such a result is in reasonably good agreement with the previous studies. This value can be viewed as a maximum value since it corresponds to the point where the final morphology does not change anymore for blends containing L-PBT7 and H-PBT10 (8 min of mixing). In the case of PBT/E-MA-GMA blends containing L-PBT45 and H-PBT42, the interfacial reaction proceeds rapidly, so that the grafting density reaches within 1–2 min a value of 0.05 chain/nm^2 (Table 4). In the same time period, a fine stable dispersion is achieved. Crosslinking of the rubber phase could of course also modify the morphology development. However, in the case of PBT/E-MA-GMA8 blends, this reaction is consecutive to the interfacial grafting reaction, so that its effect should be less important.

As previously mentioned, the PBT molecular mass does not influence the obtained results, except in the early stages of the mixing process. In the first 30 s of mixing, it is clear that the higher the PBT molecular weight, the smaller the size of the dispersed phase particles. For longer mixing times, Figs. 2 and 3 show hardly any influence of the PBT viscosity on the evolution of the blend morphology. This result can appear surprising since, for a given carboxyl chain ends concentration (in μeq/g), the higher the molecular mass, the higher the average number of carboxyl group per chain. However, as suggested in Eq. (2), the rate of interfacial reaction is directly related to the concentration of reactive groups present in the interface vicinity, i.e. in a defined volume around the interface. The concentration of carboxyl chain ends to consider is therefore the same whatever the molecular weight. The lower intrinsic reactivity of one L-PBT chain compared to one H-PBT chain is indeed compensated by the fact that, in a given volume of matter, there is a larger number of low molecular weight chains. The molecular mass of the PBT chains is also expected to influence the rate of diffusion of the chains towards the interface. This effect becomes more important at long mixing times since, in order to react at the interface, the PBT chains have indeed to diffuse through the other chains that have already reacted with the rubber particles. This diffusion is easier for the PBT with the low molecular mass. This could explain why the grafting density, Σ, after 8 min of mixing is higher for blends containing L-PBT45 than for blends containing H-PBT42. Such an explanation is however not applicable, since, in the case of a low reactive pair such as carboxyl/epoxide functionalities, the interfacial reaction is expected not to be diffusion-controlled even at long mixing times [33]. Another explanation would result from the crosslinking of the rubber phase. The epoxide groups present in the rubber phase can indeed be consumed either by the interfacial reaction or by the rubber crosslinking. The smaller the dispersed phase particles, the lower the amount of available epoxide functions per particle. In this context, one can assume that the smaller the dispersed phase particles, the faster the consumption of the epoxide groups available for reactions so that at long mixing time no further grafting of the PBT chains onto the rubber particles is possible. The effect is particularly visible for high molecular mass PBT that promotes the finest rubber dispersion.

3.2. Epoxide concentration in the rubber phase

Different routes were investigated in order to modify the epoxide concentration in the rubber phase, viz. (i) to use different commercial E-MA-GMA terpolymers containing different GMA contents, (ii) to modify part of the epoxide groups by melt mixing commercial E-MA-GMA with acid and (iii) to dilute E-MA-GMA terpolymer with non-reactive E-MA copolymer in different compositions. The results obtained by using these different strategies are presented in Section 3.3. For all blends, the matrix was constituted by M-PBT49.

3.3. M-PBT49/E-MA-GMA binary blends

Fig. 4 presents the evolution of the number average particle diameter as a function of the mixing time for M-PBT49/rubber (80/20, w/w) blends at 250 °C for three

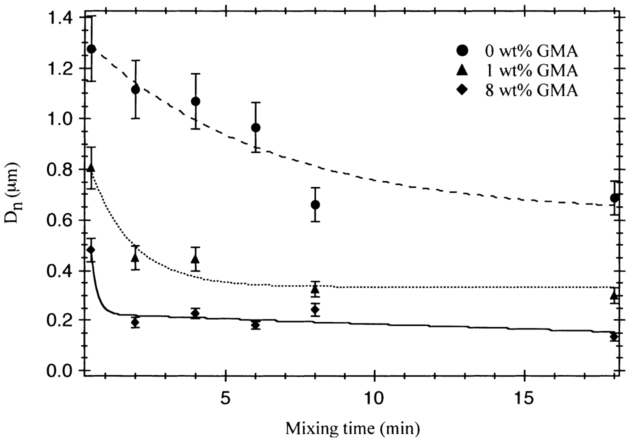


Fig. 4. Effect of the rubber GMA content on the evolution of the rubber particle size as a function of mixing time for M-PBT49/rubber (80/20, w/w) blends.

commercial rubbers. As a rule, the blend morphology becomes finer and more homogeneous as the mixing time increases. The higher the epoxide content of the rubber phase, the faster the morphology development and the finer the final dispersion. For reactive M-PBT49/E-MA-GMA blends, the number average particle size does not change anymore after 2–3 min of mixing as a result of in situ compatibilization. The formation of E-MA-GMA/PBT copolymer is expected to be more rapid for the more reactive E-MA-GMA due to a higher concentration in epoxide groups in the interface vicinity. In the case of M-PBT49/E-MA blends, the morphology development proceeds more slowly, which may be due to slow interfacial transesterification reactions between M-PBT49 and E-MA [23]. However, the extent of these reactions, if they occur at all, should be rather low since, for M-PBT49/E-MA blends, no trace of copolymer was found using the developed separation procedure.

It is surprising to note that the final particle size is intimately related to the reactivity of the E-MA-GMA chains but not to the PBT carboxyl chain end concentration. Fig. 5 shows the evolution of the number average diameter of the dispersed phase particles as a function of the interfacial grafting density Σ for both M-PBT49/E-MA-GMA8 and M-PBT49/E-MA-GMA1 blends. For M-PBT49/E-MA-GMA8 blend, a stable fine dispersion is obtained as soon as the chain area density Σ is higher than 0.05 chains/nm^2, which takes approximately 1–2 min of mixing. For M-PBT49/E-MA-GMA1 blend, the interfacial copolymer coverage is equal to 0.0085 chain/nm^2 after 8 min of mixing, which is too low to prevent coalescence. In the early stages of the blending, the amount of in situ formed copolymer is relatively small due to the low epoxide concentration in the rubber chains. Moreover, upon longer mixing time, the epoxide groups are also consumed by the crosslinking of the rubber phase. So, the amount of epoxide groups available for the interfacial reaction decreases very rapidly and consequently E-MA-GMA graft copolymers cannot be in situ formed anymore. In addition, crosslinking prevents further dispersion, so that larger rubber particles are generated. When varying the PBT carboxyl chain ends concentration, the concentrations of reactive functions in the interface vicinity would always remain high enough along the whole mixing process to allow sufficiently high interfacial copolymer coverage. In addition, crosslinking proceeds more slowly. The combination of both effects result in a finer dispersion.

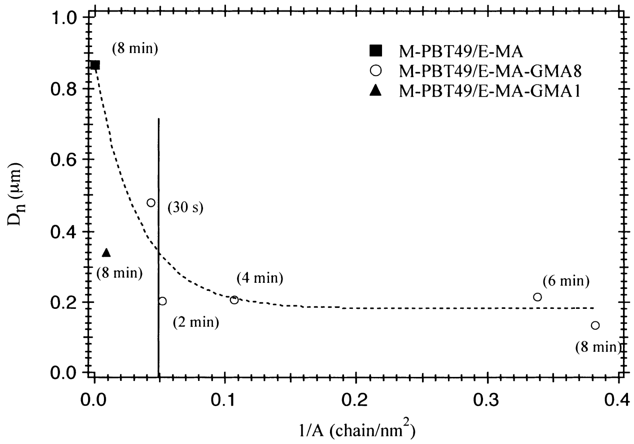


Fig. 5. Evolution of the number average diameter of the dispersed particles as a function of the chain area density Σ for M-PBT49/Rubber (80/20,w/w) blends. The corresponding mixing times are given between brackets.

3.4. M-PBT49/(E-MA-GMA/E-MA) ternary blends

Table 5 presents the morphology of M-PBT49/(E-MA-GMA/E-MA) ternary blends after 8 min of mixing for various compositions. The M-PBT49/E-MA (80/20, w/w) exhibits the general features of an uncompatibilized blend, i.e. a coarse morphology and no grafted PBT chains. Surprisingly, all the M-PBT49/(E-MA-GMA/E-MA) ternary blends exhibit the same fine dispersion. The number average diameter of the rubber particles is close to 0.15 µm independent of the amount of E-MA-GMA in the rubber phase (ranging between 100 and 25 wt%). Moreover, the polydispersity of the particle size distribution, i.e. the ratio between the volume average and the number average diameters, is not influenced by the rubber phase reactivity. The higher the epoxide content of the rubber phase, the higher the amount of M-PBT49 grafted to the rubber particles and the higher the number of chains per square nm. The effect is however less obvious for the ternary blend containing 25 wt% of E-MA-GMA.

This independence of the final blend morphology on the rubber phase composition confirms that the interfacial reaction is not limited by the diffusion of the reactive E-MA-GMA chains towards to the blend interface. This seems to be a valid assumption because of the relatively low reactivity between the epoxide functions and the carboxyl [33]. The results postulate also that only a small amount of copolymer is required to stabilize the blend morphology.

Another way to explain the above results is to consider the molecular structure of the in situ formed E-MA-GMA/PBT copolymer. In this section, the reactive rubber consisted always of E-MA-GMA terpolymer containing 8 wt% of GMA. When one E-MA-GMA chain is grafted to one M-PBT49 chain at the interface, the chance that another epoxide group of this chain reacts is high enough to prevent

Table 5
Characteristics of the M-PBT49/(E-MA-GMA/E-MA) (80/[x/20 − x], w/w) ternary blends after 8 min mixing at 250 °C and 90 rpm

wt% of E-MA-GMA in the rubber phase	100	75	50	25	0
GMA content (wt%)	8	6	4	2	0
D_n (µm)	0.15	0.13	0.17	0.14	0.66
D_v (µm)	0.19	0.17	0.21	0.18	0.77
P (%)	65.4	70.9	75.6	74.9	80.0
Σ (chains/nm^2)	0.34	0.28	0.13	0.15	0.00

another rubber chain to compete for grafting at the same interface. Therefore, the compatibilizer will have a multi-graft structure and is expected to be spread on the interface and to cover a large surface area. In these conditions, only a limited amount of reactive E-MA-GMA chains has to be present in the interface vicinity to promote efficient compatibilization of the blend and prevent dynamic coalescence. The higher copolymer density observed for M-PBT49 blends containing high E-MA-GMA content could then result from a larger amount of E-MA-GMA chains in the interface vicinity. Such process was already pointed out by Pagnoulle et al. [20] in case of slow interfacial reaction. This explanation is also supported by the results obtained in Section 2. Indeed, the use of E-MA-GMA terpolymer containing 1 wt% of GMA instead of E-MA-GMA with 8 wt% in GMA leaded to a large increase of the number average diameter of the rubber particles. In this case, no diffusion effect had to be considered since the rubber phase was not diluted with E-MA copolymer. The rubber chains should only contain around 1 epoxide group per chain so that multiple bonding between the E-MA-GMA and the M-PBT49 is not possible.

On the other hand, the extent of rubber crosslinking will be influenced by the amount of E-MA copolymer present in the rubber phase. The higher this content, the lower the crosslinking level of the rubber phase. Therefore, even if the different M-PBT49/(E-MA-GMA/E-MA) ternary blends exhibit very similar morphologies, the properties of the dispersed phase particles and the final blend properties are expected to be different.

3.5. M-PBT49/modified E-MA-GMA blends

Fig. 6 presents the evolution of the number average diameter of the rubber particles as a function of the mixing time for various M-PBT49/modified E-MA-GMA (80/20, w/w) reactive blends. Up to a modification level of 78%, these blends exhibit a very fine dispersion. The finest dispersed particles are obtained for M-PBT49 blends containing 48% modified E-MA-GMA. For modification levels above 78%, an increase of the particle size from approximately 0.2–0.4 μm is observed. In the case of modified E-MA-GMA, it was proven that there is a true competition between the two reactions and that the crosslinking reaction proceeds homogeneously throughout the dispersed phase particle [24]. The rate of the rubber crosslinking is related to the concentration in both epoxide and secondary hydroxyl groups and is expected to decrease as the modification level of the rubber chains shifts from 48 to 78%, 23% and further to 93% [23]. Fig. 6 indicates that for the applied processing conditions, the effect of rubber crosslinking on the morphology is rather limited. The number average diameter of the dispersed phase particles is rather governed by the interfacial reaction, since it increases as the concentration of epoxide groups in the rubber phase decreases. The apparent priority of the compatibilization over the rubber crosslinking is related to the processing conditions. At 90 rpm, we assume that the shear rate in the mixing chamber is sufficiently high in the early stages of the mixing to mask the difference in the crosslinking rate between the different modified E-MA-GMA [25]. As a large interfacial area is then rapidly generated, E-MA-GMA/PBT copolymers are formed at the interface, which stabilize the dispersion independently of the crosslinking of the rubber phase. For the blend containing the 93% modified E-MA-GMA, the interfacial reaction is expected to proceed slower, so that the compatibilization does not take place rapidly enough to inhibit effects due to rubber phase crosslinking and/or to dynamic coalescence. As a result, larger rubber particles are generated.

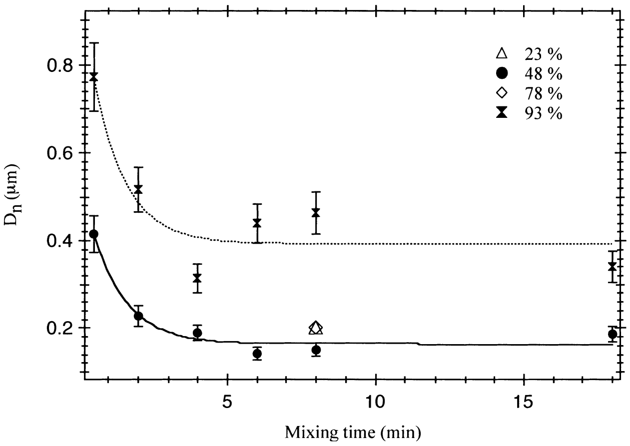


Fig. 6. Evolution of the rubber particle size as a function of the mixing time and of the modification level of the E-MA-GMA for M-PBT49/modified E-MA-GMA (80/20, w/w) blends.

At this stage, one may ask if the fine dispersion observed for the M-PBT49/48% modified E-MA-GMA blend results from the fact that the rate of the rubber crosslinking is still too slow to inhibit rubber dispersion at the early stages of the mixing or if the shear rate is sufficiently high to break the rubber network as soon as it is formed. To discriminate between those possibilities, the blending sequence was inverted. A calculated amount of 48% modified E-MA-GMA was annealed for 5 and 15 min at 30 rpm at 250 °C. Then, the M-PBT49 pellets were added for 1 min at 30 rpm to obtain a blend composition of 80/20 (w/w) M-PBT49/rubber. Finally, the screw speed was increased to 90 rpm for 8 min and the blends were analyzed by TEM. The results showed that the size of the dispersed phase particles increases from 0.15 to 0.26 μm and 0.51 μm as the pre-crosslinking time increases from 0 to 5 and 15 min, respectively. This suggests that the rubber network formed in the melt is not significantly sheared. The blend morphology is therefore intimately related to the kinetics ratio between the interface generation and the crosslinking of the rubber phase. At high shear rate, the rubber crosslinking is still too limited in the early stages of the mixing to prevent the dispersion of the rubber phase (Fig. 6).

3.6. Final considerations

Fig. 7 shows that the evolution of the number average diameter of the dispersed phase particles as a function of the mixing time for M-PBT49 blends containing E-MA-GMA (1 wt% in GMA) and 93% modified E-MA-GMA (8 wt% in GMA), respectively are almost the same. The structure of the rubber chains is expected to be quite similar. The modified E-MA-GMA chains crosslink from the early stages of the mixing, while this reaction is somewhat delayed in case of the commercial E-MA-GMA grade. However, in both cases, the extent of crosslinking should be limited according to the rather low amount of epoxide groups present on the rubber chains. So, in the early stages of the mixing, due to the high shear rate, the two systems should behave similarly and the generated morphology is then partially stabilized through interfacial coupling between the M-PBT matrix and the rubber. The effect of the crosslinking reaction only becomes significant when the dispersion has occurred so that the two systems exhibit similar morphology evolution. This is another evidence of the compatibilization over crosslinking priority.

Table 6 compares the M-PBT49/modified E-MA-GMA binary blends to the M-PBT49/(E-MA-GMA/E-MA) ternary blends with the same initial reactivity ratio [COOH]/[epoxide]. At high epoxide concentrations, no marked difference can be observed between the two systems. This is another evidence of the compatibilization over crosslinking priority. A slight deviation appears at low epoxide content in the rubber phase, i.e. the M-PBT49/(E-MA-GMA/E-MA) ternary blend presents a finer morphology than the corresponding M-PBT49/modified E-MA-GMA blend. As previously mentioned, such a difference could be attributed to the structure of the E-MA-GMA/PBT copolymer formed at the interface. The reactive chains of E-MA-GMA are expected to contain around 5–6 epoxide functions per chain incase of M-PBT49/(E-MA-GMA/E-MA) ternary blend and 1 epoxide function per chain in case of M-PBT49/modified E-MA-GMA binary blend. As a consequence, one may expect that, in case of M-PBT49/(E-MA-GMA/E-MA) ternary blend, when a (originally) E-MA-GMA is grafted to a M-PBT49 chain at the interface, the chance that another epoxide group of this chain reacts is high enough to prevent another rubber chain to compete for grafting at the same interface. Therefore, the reacted terpolymer chains are expected to have a multiple graft character and to be spread on the interface and to cover a large surface area. In contrast, the E-MA-GMA chains should be rather tethered to the interface in case of M-PBT49/modified E-MA-GMA binary blend. Such effect was particularly visible for high modification level of the E-MA-GMA chains since for lower modification level, multiple bonding between the E-MA-GMA and the M-PBT49 chains at the interface is still possible.

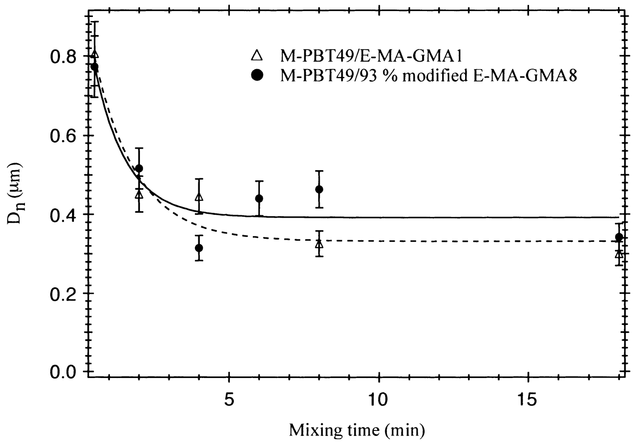


Fig. 7. Evolution of the number average diameter of the dispersed particles as a function of the mixing time for M-PBT49/E-MA-GMA (1 wt% in GMA) and M-PBT49/93% modified E-MA-GMA (8 wt% in GMA) (80/20, w/w) blends.

Table 6
Number average diameter of the rubber particles for M-PBT49/modified E-MA-GMA and M-PBT49/(E-MA-GMA/E-MA) (80/20, w/w) blends

Epoxide concentration (g GMA/g rubber)	D_n (μm)	
	M-PBT49/(E-MA-GMA/E-MA)	M-PBT49/modified E-MA-GMA
2	0.14	0.20
4	0.17	0.15
6	0.13	0.16

4. Conclusions

The influence of the reactive group concentrations on the compatibilization of PBT/epoxide-containing rubber blends has been investigated by using various PBT and E-MA-GMA grades. The interfacial reaction is slow and therefore not diffusion-controlled. The kinetics of interfacial grafting only depends on the concentration of reactive functions in the interface vicinity. The final particle size appears to be intimately related to the amount of copolymer formed in situ at the blend interface, i.e. the chain area density Σ. A value of approximately 0.05 chains/nm^2 for Σ is necessary to suppress dynamic coalescence. Two cases can be distinguished depending on the E-MA-GMA reactivity:

1. The concentration of reactive functions in the interface vicinity is not high enough during the mixing process to obtain a Σ value higher than 0.05 chains/nm^2. In this case, the dispersed particles are only partially stabilized and the final morphology results from a balance between the dynamic coalescence and the partial compatibilization and so that larger particles are generated.
2. The concentration in reactive functions in the interface vicinity is high enough during the mixing process to obtain a Σ value higher than 0.05 chains/nm^2. This case

corresponds to blends containing E-MA-GMA terpolymer with a high GMA content. In this case, it was demonstrated that

- ○ The concentration in carboxyl PBT chain ends influences the rate of compatibilization but not the final equilibrium morphology. The lower the concentration, the slower the morphology development.
- ○ PBT/(E-MA-GMA/E-MA) ($80/x/20 - x$, w/w/w) ternary blends exhibit a very fine morphology. This argues that only a very small amount of reactive chains is required to achieve the compatibilization of the blend. The obtained morphology is independent of the x value, suggesting that the diffusion of the reactive rubbers chains towards the blend interface is not the rate-limiting step for the blend compatibilization. The E-MA-GMA chains could be spread on the interface covering a large interfacial area.
- ○ In case of PBT/modified E-MA-GMA blends, the morphology development is slightly influenced by the crosslinking rate of the rubber phase at high shear rate in the mixing chamber. Changing the modification level of the rubber chains modifies also the structure of the E-MA-GMA/PBT copolymer formed at the interface during processing, which should be rather tethered to the interface in case of highly modified E-MA-GMA chains.

Acknowledgements

P.M. is very indebted to DSM n.v. for financial support and experimental facilities.

References

[1] Paul DR, Bucknall CB. Polymer blends. New York: Wiley; 1999.
[2] Fayt R, Jerome R, Teyssie P. J Polym Sci, Polym Lett Ed 1981;19:79.
[3] Fayt R, Jerome R, Teyssie P. J Polym Sci, Polym Lett Ed 1986;24:25.
[4] Xanthos M. Polym Engng Sci 1988;28:1932.
[5] Scott CE, Macosko CW. Polym Bull 1991;26:341.
[6] Favis BD. Can J Chem Engng 1991;69:619.
[7] Utracki LA. Polymer alloys and blends. New York: Carl Hanser; 1990.
[8] Pagnoulle C. PhD Thesis. University of Liège, Belgium; 2000.
[9] Van Duin M, Koning CE, Pagnoulle C, Jérôme R. Prog Polym Sci 1998;23:707.
[10] Hu G-H, Lambla M. J Polym Sci, Part A: Polym Chem 1995;33:97.
[11] Fredrickson GH. Phys Rev Lett 1996;76:3440.
[12] O'Shaughnessy B, Sawhney U. Phys Rev Lett 1996;76:3444.
[13] Fredrickson GH, Milner ST. Macromolecules 1996;29:7386.
[14] O'Shaughnessy B, Vavylonis D. Macromolecules 1999;32:1785.
[15] Yin Z, Koulic C, Pagnoulle C, Jérôme R. Macromolecules 2001;34:5132.
[16] Orr CA, Adedeji A, Hirao A, Bates FS, Macosko CW. Macromolecules 1997;30:1243.
[17] Charoensirisomboon P, Inoue T, Weber M. Polymer 2000;41:4483.
[18] De Roover B. PhD Thesis. Université Catholique de Louvain, Belgium; 1994.
[19] Dedecker K, Groeninckx G. J Appl Polym Sci 1999;73:889.
[20] Chen L, Wong B, Baker WE. Polym Engng Sci 1996;36:1594.
[21] Duvall J, Selliti C, Myers C, Hiltner A, Baer E. J Appl Polym Sci 1994;52:195.
[22] Steurer A, Hellmann GP. Polym Adv Technol 1998;9:297.
[23] Martin P, Devaux J, Legras R, van Gurp M, van Duin M. Polymer 2001;42:2463.
[24] Martin P. PhD Thesis. Université Catholique de Louvain, Belgium; 2002.
[25] Martin P, Devaux J, Legras R, Leemans L, van Gurp M, van Duin M. J Appl Polym Sci 2003; in press.
[26] Fischer M, Hellmann GP. Macromolecules 1996;29:2498.
[27] Fortelny I, Zivny A. Polym Engng Sci 1995;35:1872.
[28] Liu NC, Baker WE. Adv Polym Techol 1992;11:249.
[29] Kim JK, Kim S, Park CE. Polymer 1997;38:2155.
[30] Paul DR, Newman S, Polymer blends, vol. 2. New York: Academic Press; 1976.
[31] Macosko CW, Guéguan P, Khandpur AK, Nakayama A, Marechal P, Inoue T. Macromolecules 1996;29:5590.
[32] Jeon HK, Kim JK. Macromolecules 2000;33:8200.
[33] Fallais I. PhD Thesis. Université Catholique de Louvain, Belgium; 2001.